60 Rec'd PCT/PTO 09 JAN 2001

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED / ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		ATTORNEY'S DOCKET NUMBER P66218US0
		US APPLICATION NO (If known, see 37 CFR 1 5) 09/720259
INTERNATIONAL APPLICATION NO PCT/NO00/00157	INTERNATIONAL FILING DATE 12 May 2000	PRIORITY DATE CLAIMED 12 May 1999
TITLE OF INVENTION METHODS FOR PATTERNING POLYMER FILMS, AND USE OF THE METHODS		
APPLICANT(S) FOR DO/EO/US Olle INGANAS, Tobias NYBERG and Tomas GRANLUND		

Applicant herein submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for Internatl. Preliminary Examination was made by the 19th month from earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☒ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the Internatl. Preliminary Examination report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
    ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

    International Search Report — Swedish Patent Office
    PCT Request Form
    PCT/IB/301 Form
    PCT/IB/304 Form
    PCT/IB/308 Form
    First Page of Publication

534 Rec'd PCT/PTO 09 JAN2001

US APPLICATION NO. (if known, see 37 CFR 1.5) 09/720259	INTERNATIONAL APPLICATION NO. PCT/NO00/00157	ATTORNEY'S DOCKET NUMBER P66218US0

	CALCULATIONS	PTO USE ONLY
17. ☒ The following fees are submitted:		
Basic National Fee (37 CFR 1.492(a)(1)-(5)):		
Internatl. prelim. examination fee paid to USPTO (37 CFR 1.492 (a) (1)) . . $690.00		
No international preliminary examination fee paid to USPTO (37 CFR 1.492 (a) (2)) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) . . $710.00		
Neither international preliminary examination fee (37 CFR 1.492 (a) (3)) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO) **$1000.00**		
International preliminary examination fee paid to USPTO (37 CFR 1.492 (a) (4)) and all claims satisfied provisions of PCT Article 33(2)-(4) $100.00		
Search Report prepared by the EPO or JPO (37 CFR 1.492 (a) (5)) **$860.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 1000.00	
Surcharge of $130.00 for furnishing the **oath or declaration** later than ☒ **20** ☐ **30** months from the earliest claimed priority date (37 CFR 1.492(e)).	$ 130.00	

Claims	**Number Filed**	**Number Extra**	Rate		
Total Claims	**25** - 20 =	-5-	x $18.00	$ 90.00	
Independent Claims	**2** - 3 =	-0-	x $80.00	$	
Multiple Dependent Claim(s) (if applicable)			+ $270.00	$	
TOTAL OF ABOVE CALCULATIONS =				$ 1220.00	
Reduction by 1/2 for filing by **small entity**, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$	
SUBTOTAL =				$ 1220.00	
Processing fee of $130 for furnishing the **English translation** later than ☐ **20** ☐ **30** months from the earliest claimed priority date (37 CFR 1.492(f))				$	
TOTAL NATIONAL FEE =				$ 1220.00	
Fee of $40.00 for recording the enclosed **assignment** (37 CFR 1.21(h)). Assignment must be accompanied by appropriate cover sheet (37 CFR 3.28, 3.31).				$	
TOTAL FEES ENCLOSED =				$ 1220.00	
				Amt. to be refunded:	$
				Amt. charged:	$

a. ☒ A check in the amount of $ 1220.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. **06-1358** in the amount of $ ____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge my account any additional fees set forth in §1.492 during the pendency of this application, or credit any overpayment to Deposit Account No. **06-1358**. A duplicate copy of this sheet is enclosed.

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JPH&S 3/95

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Olle INGANAS et al.

Serial No.: new

Filing Date: January 9, 2001

For: METHODS FOR PATTERNING POLYMER FILMS, AND USE OF THE METHODS

PRELIMINARY AMENDMENT TO LESSEN FEES

Assistant Commissioner of Patents
Washington, D.C. 20231

Sir:

Prior to initial examination, please amend the above-identified application as follows:

IN THE CLAIMS

Claim 25, line 1, delete "claims 1 or 14",
insert --claim 1--.

REMARKS

The foregoing Preliminary Amendment is requested in order to delete the multiple dependent claims and avoid paying the multiple dependent claims fee.

Early action on the merits is respectfully requested.

Respectfully submitted,

JACOBSON, PRICE, HOLMAN & STERN, PLLC

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Atty. Docket: P66218US0
Date: January 9, 2001
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534 Rec'd PCT/PTO 09 JAN2001

Methods for patterning polymer films, and use of the methods

The present invention concerns a method for patterning a polymer film forming a coating on a material surface, wherein the patterning takes place by means of a stamp having a surface with at least one indentation formed therein, and a method for transferring a patterned polymer film onto a material surface by means of a stamp having a surface with at least one indentation formed therein. The invention also concerns the use of methods of this kind.

The use of conjugated polymers in electronic devices requires means for processing them into patternable thin films. Patterning conducting electrodes and semiconducting polymers in polymer diodes requires patterning of all materials, at a resolution of 0.1-50 μm. This can possibly be accomplished by the use of classical photolithography with help of photoresists, but several new problems arise in the chemical etching of the material and the chemical compatibility with conventional photoresists. It would therefore be desirable to pattern this material with non-photolithographic techniques.

A new method for patterning is based on elastomeric stamps. Patterning of a surface here requires conformal contact between the stamp and surface. Many variants of these techniques are documented, in particular in the work from G. Whitesides' group at Harvard University (Y. Xia and G. Whitesides, Soft lithography, Angewandte Chemie-International Edition in English 37(5): 551-575 (1998) and Y. Xia and G. Whitesides, Soft lithography, Annual Review of Materials Science, 28:153-184 (1998)).

The work of Whitesides' group is disclosed in US patent No. 5 512 131, titled "Formation of microstamped patterns on surfaces and derivative articles" (Kumar & Whitesides). This prior art document discloses a method of patterning a material surface, comprising steps of providing a stamp having a surface including at least one indentation formed therein, said indentation configured with a stamping surface defining a first pattern; coating said stamping surface with a molecular species terminating at the first end in a functional group selected to bind to said material; processing said stamping surface in a first orientation and contacting a portion of said material surface with said stamping surface to hold said molecular species against said material surface portion to allow said functional group to bind thereto; and removing said stamping surface to provide a self-assembled

molecular species on said material surface according to said first pattern in said first orientation.

This prior art disclosure amounts to a process wherein a chemical species capable of forming a self-assembled monolayer is coated onto the stamping surface of an elastomeric stamp, said species having a functional group selected to bind to a particular material. The stamping surface is placed against a surface of a material surface and removed to leave a self-assembled monolayer of the species according to the stamping surface pattern of the stamp.

Further there is known a number of different prior art techniques for patterning surfaces or materials deposited thereon without having to resort to conventional photolithography.

As a further example of prior art a paper by Zhang, L.G.; Liu, J.F. and Lu, Z.H., titled "Microfabrication on polymer with a contact procedure", Supramolecular Science, Vol. 5, Nos. 5-6:713-715 (Oct-Dec. 1998) discloses the fabrication of thickness-contrast micropatterns based on a contact procedure. Polymer (polydimethylsiloxane) micropost arrays are fabricated with grids as the masters. This contact procedure, which does not rely on etching, extends the present limits of microfabrication. In addition the thickness-contrast micropatterns on the polymer can be replicated to other substrates, such as silicon wafers, with microcontact printing.

These techniques that are collected in the catchall term soft lithography are based on pattern transfer by a soft rubber stamp in direct contact with the surfaces and materials to be patterned. Soft lithography includes microcontact printing (μCP), replica molding (REM) and micromolding in capillaries (MIMIC). The patterning technique is based on physical contact, not the projection of light through a mask, as in photolithography. The fundamental limits to resolution are due to the range of the van der Waals forces determining the interaction of surfaces (~10 nm), not the diffraction of light in far-field geometries (~0.5 μm).

An important element of microcontact printing (μCP) is the formation, by selfassembly, of a monomolecular layer of etch resistant organic molecules. Alkanethiols are the preferred species, which chemisorb into molecular thin films on Au, Ag, Cu and other metal surfaces. They form layers of very small

thickness (1-3 nm) which are tightly bound (but can be desorbed at high temperatures and by exchange). These alkane layers are used as the resist; a metal layer is protected from etching below the molecular film, and where it is not deposited the metal is removed. The patterning of the resist layer is in its turn done with molecular stamps. A poly(dimethylsiloxane) (PDMS) layer, patterned with protruding and recessed elements in a prior step, is exposed to a solution of alkanethiols; the rubbery stamps are pressed onto a surface for a short time; alkanethiols react with the gold surface when close contact is obtained; and a pattern of protected and non-protected Au is obtained. This layer is now exposed to another alkanethiol, adsorbing from solution onto the unprotected gold surface. A patterned layer is obtained. The process is called microcontact printing (μCP). It has been established that formation of the patterned structure occurs within a few seconds.

The patterned layer may now be used as ultrathin resists in selective wet etching, or as templates for the control of wetting, dewetting, nucleation and growth or deposition of other materials. Minimal sizes of 35 nm trenches in Au layers have been obtained with etching techniques.

Patterned self-assembled monolayers (SAMs) allow control of the local hydrophobic/hydrophilic nature of the surface, and therefore act to control the deposition of materials. Water will condense on the hydrophilic part of the surface; this allows us to deposit materials from water solution onto a patterned surface in a regular fashion. Likewise, organic polymers may be deposited onto the hydrophobic surfaces from organic solvents. Both these approaches allow the formation of patterned structures of deposited material. Selective chemical vapour deposition (CVD) processes onto SAMs controlling the nucleation behaviour is another approach for pattern formation in ceramics and metals. Proteins and cells can be selectively adsorbed on patterned surfaces.

It is easy to pattern non-planar surfaces with this approach, a near impossibility with photolithography. Capillaries of radius of curvature 50 μm have been patterned with structures of dimensions down to a few microns. This enables the construction of more complex structures on patterned and non-planar surfaces, relieving one of the tyranny of planar photolithography.

The microcontact printing is simple, inexpensive and flexible. With bigger structures (>20 μm) clean room facilities are not necessary. The stamp can be

used and reused many times, providing high fidelity reproduction. Because the master structure is normally used as a template to prepare "negatives" (as it were), one can form many identical stamps from a single master, and each one of them can be used some hundred times - multiple copying and parallel processing of the structures is therefore possible. The capital cost of producing the structures is very low. The fabrication of masters of course requires other lithographical techniques, such as photolithography or electron beam lithography, but the multiplication of stamps gives parallel production lines. Micromolding is a small twist to classical molding in that a soft and flexible silicone rubber is used, rather than a hard mold. The elasticity and low surface energy of this mold material allows it to be removed easily from the prepared structure. Replica-molding (REM) can be obtained down to the 30 nm dimensions. Such methods may be used to prepare optical structures as in gratings, microlenses, Fresnel lenses and similar designs for the diffraction and refraction of light. Microprinting is best obtained with the technique named micro-transfer molding (μTM) where a patterned mold is filled with a liquid prepolymer, excess liquid removed and the mold pressed against a surface, irradiated or heated to polymerize. After the liquid precursor is converted into a solid, the mold is peeled away. In a slight modification of this technique (micromolding in capillaries, MIMIC) connected structures are placed in contact with low viscosity liquids, which fill the channels by capillary action. These liquids may carry nanoparticles, or solutions for solgel conversion, or polymers in solution. After conversion of the liquid to a solid, the mold is removed. Processing of the resulting structure by photochemistry or thermal treatment is now possible, for instance converting a precursor to carbon materials. The remaining structure may now be the functional element - such as an optical waveguide - or a resist to be used to etch the underlying material. In a slight twist to this method, SAMIM (solvent assisted MIMIC), a solvent is used to modify the sample surface to be patterned, and the patterned is defined with a micromold in which the structure is defined.

The very important aspect of faithful reproduction over large areas and with low defect density is not yet fully resolved. In a recent report from IBM Zurich, it is claimed that structures of 1 micrometer pitch were faithfully replicated without defects over areas of 10 cm^2, using μCP or MIMIC.

Patterning of monolayers of molecules is the most elegant and novel of these prior art methods, but is limited to transfer of monolayers, subsequently used for etch resists and surface activating elements. Transfer of polymer patterns is normally done with MIMIC and microcontact printing. In MIMIC a polymer precursor is patterned by filling channels defined by applying a stamp onto a surface; in microcontact printing a polymer (precursor) fills the channels turned upside down, in such a way as to form the structure which is then transferred to the surface. Transfer of polymer layers to functionally modified surfaces has been reported; see L. Yan, W.T.S. Huck, X.M. Zhao, and G.M. Whitesides, Patterning thin films of poly(ethylene imine) on a reactive SAM using microcontact printing, Langmuir, 15(4): 1208-1214 (1999).

The patterning of polymers, and in particular conjugated polymers has been reported (see Z. Huang, P.C. Wang, J. Feng, A.G. MacDiarmid, Y. Xia, and G.M. Whitesides, Selective deposition of films of polypyrrole, polyaniline and nickel on hydrophobic/hydrophilic patterned surfaces and applications, Synthetic Metals, 85(1-3):1375-1376 (1997); and Z.Y. Huang, P.C. Wang, A.G. MacDiarmid, Y.N. Xia, and G. Whitesides, Selective deposition of conducting polymers on hydroxyl-terminated surfaces with printed monolayers of alkylsiloxanes as templates, Langmuir 13(24):6480-6484 (1997)) using hydrophobic/hydrophilic modification of monomer adhesion. It may be difficult to deposit high quality polymers from dispersions and solutions with the materials used in these stamps; in particular, the swelling of a poly(dimethylsiloxane) stamp in chloroform prevents the patterning of many of the luminescent polymers used for electroluminescent polymer displays where patterning is desired. These polymers are often solvated in solvents such as chloroform. Likewise, the patterning of water-soluble polymers prohibits the use of some soft lithography techniques, such as MIMIC (Y. Xia and G. Whitesides, Soft lithography, Angewandte Chemie-International Edition in English 37(5): 551-575 (1998) and Y. Xia and G. Whitesides, Soft lithography, Annual Review of Materials Science, 28:153-184 (1998)) as the solvent is required to pass through an elastomeric membrane. Chloroform will swell the stamp, and destroy the fine pattern to be transferred; in the other extreme, water is not easily transported through the extremely non-polar elastomeric stamp, and pattern transfer will be prohibited. Novel patterning methods are therefore desired.

In regard of certain drawbacks and limitations of the above-mentioned prior art methods, it is thus an object of the present invention to provide methods whereby patterns can be generated in thin films of polymer deposited on material surface by a simple and inexpensive technique based on the use of a specially designed stamp for generating the patterns. Particularly it is another object of the present invention to be able to pattern thin film of polymers which initially form continuous layers and moreover exhibit advantageous electronic or optical properties, e.g. for use as pattern electrodes or pixels in optoelectronic displays.

Finally, it is also an object of the invention to provide patterned thin films of polymer on a substrate in order to facilitate specific processing of the substrate.

The above-mentioned objects and advantages are realized with a method for patterning a polymer film according to the invention the method being characterized by depositing onto the material surface a thin film of polymer, applying to the material surface the stamp made of an elastomeric material in conformal contact with the surface of the thin film, such that portions thereof contacting one or more protruding elements of the elastomeric stamp, the formed by the at least one indentation thereof, are attached to the protruding element or elements and removed from the material surface with the stamp.

According to the invention the polymer can advantageously be modified by incorporating additives in order to reduce the cohesive binding of the polymer film, in which case an additive can be a water-soluble organic compound, or selected among ethylene glycol, poly(ethylene glycol), glycerol, sorbitol, polyol, or any combinations thereof.

According to the invention the polymer can be a water-soluble or dispersed polymer, or a conducting conjugated polymer in its doped or undoped state, or poly(3,4-dioxyethylenethiophene) (PEDOT) or deriving from a copolymer thereof, or one or more mixtures incorporating the monomer (EDOT) form.

According to the invention it is advantageous modifying the material surface in order to provide a weak adhesion between the material surface and the polymer film to be removed therefrom, and then preferably modifying the material surface by plasma etching.

According to the invention it is also advantageous modifying the elastomer stamp surface in order to provide a strong adhesion between the stamp and the polymer film to be attached thereto, and then preferably modifying the elastomer stamp surface by plasma etching.

Finally it is according to the method of the invention advantageous enhancing the adhesion between stamp and polymer film by means of additives to the latter, an additive then preferably being glycerol.

The above-mentioned object and advantages are also realized according to the present invention with a method for transferring a polymer film, the method being characterized by depositing onto the stamp surface a thin film of polymer, applying the stamp made of an elastomeric material in conformal contact with the material surface, such that the thin film of polymer is transferred thereto from one or more protruding elements of the elastomeric stamp formed by the at least one indentation thereof, and leaving a patterned thin film of polymer on the material surface when removing the stamp therefrom.

In the above method according to the invention it is advantageous modifying the polymer film by incorporating additives in order to reduce the cohesive binding of the polymer film, the additive then preferably being a water-soluble organic compound, or preferably selected an additive among ethylene glycol, poly(ethylene glycol), glycerol, sorbitol, polyol, or any combinations thereof.

In the above method according to the invention it is advantageous that the polymer film is a water-soluble or dispersed polymer, or that the polymer is a conducting conjugated polymer in its doped or undoped state, or poly(3,4-dioxyethylenethiophene) (PEDOT) or deriving from a copolymer thereof, or one or more mixtures incorporating the monomer (EDOT).

In the above method according to the invention it is advantageous modifying the elastomer stamp surface in order to provide a weak adhesion between the elastomer surface and the polymer film to be removed therefrom, and then preferably modifying the elastomer stamp surface by plasma etching.

In the above method according to the invention it is advantageous modifying the material surface in order to provide a strong adhesion between the

material surface and the polymer film to be transferred thereto, and then preferably modifying the material surface by plasma etching.

Finally the above mentioned objects and advantages are provided with the use of the method for patterning or the method for transferring to provide a patterned etch resist in the form of a thin film of polymer on a gold layer, whereby the gold layer can be removed by etching of the area unprotected by the resist, the polymer preferably being PEDOT.

Further features and advantages of the method according to the invention are apparent from the appended dependent claims.

The invention shall now be described in a general manner and in connection with the appended drawing figures in case of one of the methods, as well as with a reference to exemplary embodiments of both the methods.

In the drawing figures,

fig. 1 shows the deposition of a thin film of polymer on a substrate,

fig. 2 the application of a stamp to the thin film polymer, and

fig. 3 schematically the patterning of the thin film of the polymer.

A particular polymer of great interest in these devices is the poly(3,4-dioxoethylenethiophene) (PEDOT) which is a commercial polymer from Bayer AG. It is produced in the form of an aqueous dispersion, and can be coated, e.g. spin-coated onto a surface to form a thin film. This film has very attractive properties for polymer electronic devices as it for instance enhances the stability and efficiency of polymer light emitting diodes, or the hole collection in polymer photodiodes, or the hole injection in metal/PEDOT/polymer structures. It is, however, difficult to pattern this polymer dispersion with the hydrophobic polydimethylsiloxane (PDMS) stamp in the MIMIC method. Thus the present invention provides alternative methods of patterning PEDOT films.

One of the requirements for the use of this patterned film is that sufficient electrical conductivity can be obtained to allow the polymer to be used as the electrode in devices. Surprisingly, the patternable film is obtained with similar additives which has been shown to give enhanced electrical conductivity, up to 80 S/cm, after thermal curing.

In these methods according to the present invention, a film of modified PEDOT is deposited on the surface to be patterned by spin coating, and patterning is done by removing parts of the film with a suitable elastomer stamp. This is the first method according to the invention and shall subsequently be termed "Lift-up". In the alternative method, a modified PEDOT layer is deposited on the stamp and then transferred onto the surface to be patterned. This is the second method according to the invention and subsequently termed "Put-down".

These methods are superior to prior art in that they allow patterning of very large areas on (non-planar) surfaces. It is documented in the literature (see Y. Xia and G. Whitesides, Soft lithography, Angewandte Chemie-International Edition in English 37(5): 551-575 (1998); and Y. Xia and G. Whitesides, Soft lithography, Annual Review of Materials Science, 28:153-184 (1998)) that polymers can be deposited onto surfaces in patterns with MIMIC, in which indentations in a stamp act as channels to allow capillary filling with some polymer solution or precursor polymer. This requires that all areas to be filled are connected; an isolated pixel cannot be filled by capillary action. MIMIC will also require long filling time, as the size of channels is reduced and length increased. It is therefore not suited for reel-to-reel production. Both the methods according to the invention are in principle compatible with reel-to-reel production, and also allow the patterning of isolated structures.

They are also superior in that the patterning of the polymer layer does not (necessarily) require the previous patterning of the surface, as for instance in Z. Huang, P.C. Wang, J. Feng, A.G. MacDiarmid, Y. Xia, and G.M. Whitesides, Selective deposition of films of polypyrrole, polyaniline and nickel on hydrophobic/hydrophilic patterned surfaces and applications, Synthetic Metals, 85(1-3):1375-1376 (1997); and Z.Y. Huang, P.C. Wang, A.G. MacDiarmid, Y.N. Xia, and G. Whitesides, Selective deposition of conducting polymers on hydroxyl-terminated surfaces with printed monolayers of alkylsiloxanes as templates, Langmuir 13(24):6480-6484 (1997), and that polymers, not monomers, are deposited.

The preparation of the modified polymer is done in order to tune the cohesive energy of the film, which has to allow the rupturing of the film in both methods; it is also done to tune adhesion to the substrate and/or stamp. The

internal cohesion of the film is modified by adding low molecular species in the present case, but could in general be any additive giving this function. It is, of course, essential that the additives are in no way detrimental to the function of the layer, and in the present case the additives are actually beneficial to the function.

When considering the advantages of these methods, we note that Lift-up and Put-down are complementary in the sense that where the former fails, the latter should work. Poor adhesion of the film to be patterned to the substrate suggests that Lift-up should be used; poor adhesion to the stamp suggests that Put-down could be used.

In Lift-up, the polymer film transfer between stamp and surface is used to pick up parts of a PEDOT film from a substrate, by attaching an elastomeric stamp onto the thin film of PEDOT on a fully covered substrate. The molecular contact between film and stamp breaks up the film, and it can now be micropatterned to any topology by this method. The PEDOT film will also now be prepared with the help of additives, and after transfer the film is cured/converted to a higher conductivity by thermal treatment. Features of dimensions down to 10 µm can easily be patterned. One of the advantages of this technique as compared to MIMIC is that isolated PEDOT pixel can be defined. In this method no solvent is used, which increases the number of materials that can be patterned.

Specifically fig. 1 relates to the lift-up and shows how a PEDOT film is spin deposited on the substrate. In a second step shown in fig. 2 a plasma etched poly(dimethylsiloxane) stamp is applied to the thin film and simultaneously heated. The stamp may be plasma etched to obtain an adhesion between the thin film and the stamp which is stronger than the adhesion between the thin film and the substrate. In the subsequent and final step in the Lift-up process, shown in fig. 3, the stamp is lifted and the thin-film polymer in the form of PEDOT adheres to the protruding portion of the stamps, such that the pattern is formed in the thin film PEDOT on the substrate when the stamp is removed.

In Put-down a slightly modified PEDOT dispersion is coated onto an elastomeric stamp by spin coating. By adding a low molecular weight compound such as ethylene glycol, glycerol or sorbitol in the dispersion, the surface remains sticky enough to attach to another surface brought close. For

structures with a large enough spacing between the protruding parts this is sufficient to transfer the PEDOT residing on the upper edge of the structure onto a mating surface, at the right temperature and pressure. With the use of the Put-down method one may be able to transfer films with structures smaller than 100 µm. This method has the added advantage that no limitation to the topology is caused from the filling of channels with liquid, such as in the MIMIC process. There is also the advantage that the surface to be coated does not need to be planar; actually non-even surfaces can be handled.

It shall now be examples of particularly preferred embodiments according to the invention, including both the lift-up and the put-down processes.

Example 1: Lift-up

Poly(3,4-dioxymethylenethiophene)-polystyrenesulfonate (PEDOT-PSS) (Baytron from Bayer AG) is mixed with glycerol to make a 1:2 weight ratio mixture. The mixture is spin-coated into a thin continuous layer on a glass surface. An elastomer stamp formed in poly(dimethylsiloxane) (Sylgard 184, Dow Corning) is plasma-treated for 10 to 30 s in an oxygen plasma. The relief-patterned stamp is brought in conformal contact with the layer, which is then heated to 50-100° C for 15 to 60 s and subsequently removed with the removal of the elastomer stamp. – As an alternative to glycerol sorbitol could be used, but apparently sorbitol mixed PEDOT-PSS works poorly if at all with Lift-up.

Example 2: Lift Up

PEDOT-PSS (Baytron from Bayer AG) is mixed with glycerol to make a 1:1 weight ratio mixture. The mixture is spin-coated into a thin continuous layer on a glass surface. An elastomer stamp formed in poly(dimethylsiloxane) (Sylgard 184, Dow Corning) is plasma-treated for 10 to 30 s in an oxygen plasma. The relief-patterned stamp is brought in conformal contact with the layer, which is then heated to 50-100° C for 15 to 60 s and subsequently removed with the removal of the elastomer stamp.

Example 3: Put-down

PEDOT-PSS (Baytron from Bayer AG) is mixed with ethylene glycol to make a 1:1 molar ratio mixture. An elastomer stamp formed in poly(dimethylsiloxane) (Sylgard 184, Dow Corning) is plasma-treated for 10 s in an oxygen plasma. The relief-patterned stamp is dipped into the mixture and dip-coated. It is brought in conformal contact with an ITO

surface and part of the layer is deposited from the stamp onto the ITO, leaving a layer of patterned PEDOT-PSS mixture.

Example 4: Put-down

PEDOT-PSS (Baytron from Bayer AG) is mixed with ethylene glycol to make a 1:1 molar ratio mixture. An elastomer stamp formed in poly(dimethylsiloxane) (Sylgard 184, Dow Corning) is plasma-treated for 10 s in an oxygen plasma. The relief-patterned stamp is dip-coated with the mixture. It is brought in conformal contact with an Au surface and part of the layer is deposited from the stamp onto the Au, leaving a layer of patterned PEDOT-PSS mixture.

Example 5: Put-down

PEDOT-PSS (Baytron from Bayer AG) is mixed with glycerol to make a 1:1 molar ratio mixture. An elastomer stamp formed in poly(dimethylsiloxane) (Sylgard 184, Dow Corning) is plasma-treated for 10 s in an oxygen plasma. The relief-patterned stamp is dip-coated with the mixture. It is brought in conformal contact with a Cu surface and part of the layer is deposited from the stamp onto the Cu, leaving a layer of patterned PEDOT-PSS mixture.

Example 6: Put-down

PEDOT-PSS (Baytron from Bayer AG) is mixed with glycerol to make a 1:1 molar ratio mixture. An elastomer stamp formed in poly(dimethylsiloxane) (Sylgard 184, Dow Corning) is plasma-treated for 10 s in an oxygen plasma. The relief-patterned stamp is dip-coated with the mixture. It is brought in conformal contact with a glass surface and part of the layer is deposited from the stamp onto the glass, leaving a layer of patterned PEDOT-PSS mixture.

Example 7: Put-down

PEDOT-PSS (Baytron from Bayer AG) is mixed with glycerol to make a 1:1 molar ratio mixture. An elastomer stamp formed in poly(dimethylsiloxane) (Sylgard 184, Dow Corning) is plasma-treated for 10 s in an oxygen plasma. The relief-patterned stamp is dip-coated with the mixture. It is brought in conformal contact with an Au surface and part of the layer is deposited from the stamp onto the Au, leaving a layer of patterned PEDOT-PSS mixture. The decorated Au surface is exposed to an etchant (gold etch solution: 5g I_2, 10 g KI dissolved in 250 ml H_2O) to remove the unprotected Au layer.

PATENT CLAIMS

1. A method for patterning a polymer film forming a coating on a material surface, wherein the patterning takes place by means of a stamp having a surface with at least one indentation formed therein, characterized by depositing onto the material surface a thin film of polymer, applying to the material surface the stamp made of an elastomeric material in conformal contact with the surface of the thin film, such that portions thereof contacting one or more protruding elements of the elastomeric stamp formed by the at least one indentation thereof are attached to the protruding element or elements and removed from the material surface with the stamp.

2. A method according to claim 1, characterized by modifying the polymer film by incorporating additives in order to reduce the cohesive binding of the polymer film.

3. A method according to claim 2, characterized by an additive being a water-soluble organic compound.

4. A method according to claim 2, characterized by an additive being selected among ethylene glycol, poly(ethylene glycol), glycerol, sorbitol, polyol, or any combinations thereof.

5. A method according to claim 1, characterized by the polymer being a water-soluble or dispersed polymer.

6. A method according to claim 1, characterized by the polymer being a conducting conjugated polymer in its doped or undoped state.

7. A method according to claim 1, characterized by the polymer being poly(3,4-dioxyethylenethiophene) (PEDOT) or deriving from a copolymer thereof or one or more mixtures incorporating the monomer (EDOT) form.

8. A method according to claim 1, characterized by modifying the material surface in order to provide a weak adhesion between the material surface and the polymer film to be removed therefrom.

9. A method, according to claim 8, characterized by modifying the material surface by plasma etching.

10. A method according to claim 1, characterized by modifying the elastomer stamp surface in order to provide a strong adhesion between the stamp and the polymer film to be attached thereto.

11. A method according to claim 9, characterized by modifying the elastomer stamp surface by plasma etching.

12. A method according to claim 1, characterized by enhancing the adhesion between stamp and the polymer film by means of additives to the latter.

13. A method according to claim 12, characterized by an additive being glycerol.

14. A method for transferring a patterned polymer film onto a material surface by means of a stamp having a surface with at least one indentation formed therein, characterized by depositing onto the stamp surface a thin film of polymer, applying the stamp made of an elastomeric material in conformal contact with the material surface, such that the thin film of polymer is transferred thereto from one or more protruding elements of the elastomeric stamp formed by the at least one indentation thereof, and leaving a patterned thin film of polymer on the material surface when removing the stamp therefrom.

15. A method according to claim 14, characterized by modifying the polymer film by incorporating additives in order to reduce the cohesive binding of the polymer film.

16. A method according to claim 15 , characterized by an additive being a water soluble organic compound.

17. A method according to claim 15, characterized by an additive being selected among ethylene glycol, poly(ethylene glycol), glycerol, sorbitol, polyol, or any combinations thereof.

18. A method according to claim 14, characterized by the polymer being a water-soluble or dispersed polymer.

19. A method according to claim 14, characterized by the polymer being a conducting conjugated polymer in its doped or undoped state.

20. A method according to claim 14, characterized by the polymer being poly(3,4-dioxyethylenethiophene) (PEDOT) or deriving from a copolymer thereof or one or more mixtures incorporating the monomer (EDOT).

21. A method according to claim 14, characterized by modifying the elastomer stamp surface in order to provide a weak adhesion between the elastomer surface and the polymer film to be removed therefrom.

22. A method according to claim 21, characterized by modifying the elastomer stamp surface by plasma etching.

23. A method according to claim 14, characterized by modifying the material surface in order to provide a strong adhesion between the material surface and the polymer film to be transferred thereto.

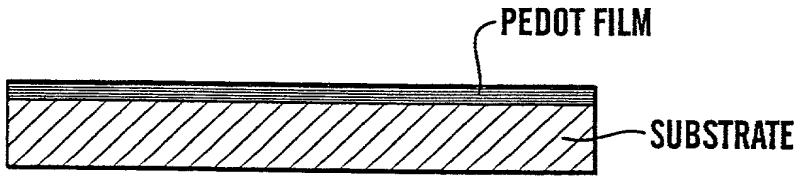
24. A method according to claim 23, characterized by modifying the material surface by plasma etching.

25. The use of a method according to claims 1 or 14 to provide a patterned etch resist in the form of a thin film of polymer on a gold layer, whereby the gold layer can be removed by etching of the area unprotected by the resist, the polymer preferably being PEDOT.

Abstract

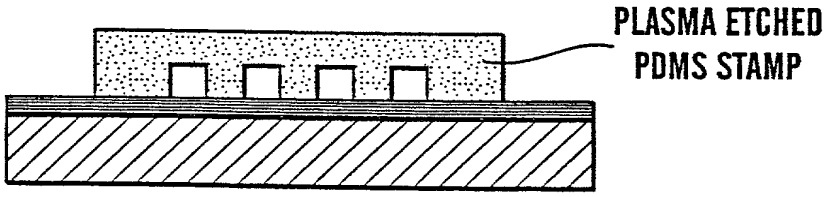
In a method for patterning a polymer film forming a coating on a material surface, a thin film of polymer is deposited on the surface and the patterning takes place by applying to the material surface a stamp made of an elastomeric material in conformal contact with the surface of the thin film, such that portions thereof contacting one or more protruding elements of the elastomeric stamp formed by one or more indentations thereof, are attached to the protruding element or elements and removed from the material surface with the stamp. In a method for transferring a patterned polymer film onto a material surface, a thin film polymer is deposited on a stamp surface and the stamp is applied in conformal contact with the material surface, such that thin film of polymer is transferred thereto from one or more protruding elements of the elastomeric stamp formed by at least one indentation thereof, thus leaving a patterned thin film of polymer on the material surface when removing the stamp therefrom. Use for patterning an etched resist in the form of a thin film of polymer on a gold layer.

1/1



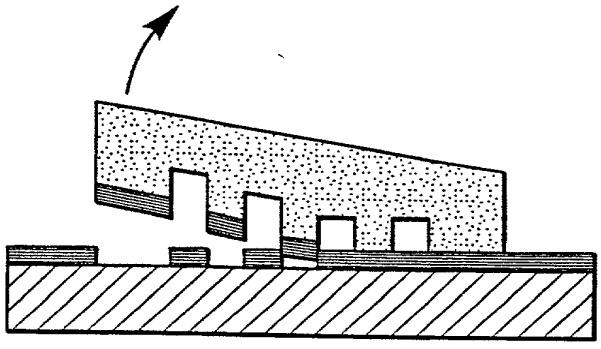
SPIN PEDOT FILM ON SUBSTRATE

Fig.1



APPLY STAMP AND HEAT

Fig.2



PEEL OFF STAMP AND STAMP-ADHERED PEDOT

Fig.3

DECLARATION AND POWER OF ATTORNEY U.S.A.

ALL PATENTS, INCLUDING DESIGN
FOR APPLICATION BASED ON PCT, PARIS CONVENTION;
NON PRIORITY; OR PROVISIONAL APPLICATIONS

FOR ATTORNEYS' USE ONLY
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101 / 102

As a below named inventor, I declare that my residence, post office address and citizenship are stated below next to my name, the information given herein is true, that I believe that I am the original, first and sole inventor (if only one name is listed at 201 below), or an original, first and joint inventor (if plural inventors are named below at 201-203, or on additional sheets attached hereto) of the subject matter which is claimed and for which patent is sought on the invention entitled:

Methods for patterning polymer films, and use of the methods

which is described and claimed in:

[X] PCT International Application No. PCT/NO00/00157 filed 12 May 2000

[ ] the attached specification

[ ] the specification in application Serial No. _____ filed _____

(if applicable) and amended on _____

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.
I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.
I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

103 / 104

Prior Foreign Application(s)

(Number)	(Country)	(Day/Month/Year Filed)	Priority Claimed Yes	No
19992295	Norway	12 May 1999	[X]	[ ]
			[ ]	[ ]
			[ ]	[ ]

I hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional application(s) listed below:

Application No. _____ Filing Date _____ Application No. _____ Filing Date _____

105

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status: patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorneys (Registration No.) to prosecute this application, receive and act on instructions from my agent, and transact all business in the Patent and Trademark Office connected therewith. HARVEY B. JACOBSON, JR. (20,851); D DOUGLAS PRICE (24,514); JOHN CLARKE HOLMAN (22,769); MARVIN R. STERN (20,640); ALLEN S. MELSER (27,215); MICHAEL R. SLOBASKY (26,421); JONATHAN L. SCHERER (29,851); IRWIN M AISENBERG (19,007); WILLIAM E. PLAYER (31,409); YOON S. HAM (45,307) and NATHANIEL A. HUMPHRIES (22,772).

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Inventor(s) name must include at least one unabbreviated first or middle name.

201	FULL NAME * OF INVENTOR	FAMILY NAME: Inganäs	GIVEN NAME: Olle	MIDDLE NAME		
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	POST OFFICE ADDRESS	POST OFFICE ADDRESS: Wernersgatan 13	CITY: S-582 46 Linköping	STATE OR COUNTRY: Sweden SEX	ZIP CODE: 582 46	
202	FULL NAME * OF INVENTOR	FAMILY NAME: Nyberg	GIVEN NAME: Tobias	MIDDLE NAME		
	RESIDENCE & CITIZENSHIP	CITY: LINKÖPING	STATE OR FOREIGN COUNTRY: SWEDEN	COUNTRY OF CITIZENSHIP: SWEDEN SEX		
	POST OFFICE ADDRESS	POST OFFICE ADDRESS: Solrosgatan 4A	CITY: S-582 46 Linköping	STATE OR COUNTRY: Sweden	ZIP CODE: 582 46	
203	FULL NAME * OF INVENTOR	FAMILY NAME: Granlund	GIVEN NAME: Tomas	MIDDLE NAME		
	RESIDENCE & CITIZENSHIP	CITY: LINKÖPING	STATE OR FOREIGN COUNTRY: SWEDEN	COUNTRY OF CITIZENSHIP: SWEDEN SEX		
	POST OFFICE ADDRESS	POST OFFICE ADDRESS: Arrendegatan 23	CITY: S-583 31 Linköping	STATE OR COUNTRY: Sweden	ZIP CODE: 583 31	

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under section 1001 of Title 18 of the United States Code; and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201*	SIGNATURE OF INVENTOR 202*	SIGNATURE OF INVENTOR 203*
		Thomas Granlund
DATE 20010122	DATE 2000 Dec 25	DATE 2001-01-16

[ ] Additional inventors are named on separately numbered sheets attached hereto.

UNITED STATES OF AMERICA - ASSIGNMENT

(1-5) *Insert Name(s) of Inventors*

(1) Olle INGANÄS

(2) Tobias NYBERG

(3) Tomas GRANLUND

(4) ..... and

(5) .....

In consideration of the sum of one dollar ($1.00), and other good and valuable considerations paid to each of the undersigned, the receipt and sufficiency of which are hereby acknowledged, the undersigned hereby assigns, transfers and sets over to

(6) *Insert Name of Assignee* — (6) Thin Film Electronics ASA

(7) *Insert Address of Assignee* — (7) of P.O.Box 1872 Vika, N-0124 OSLO NORWAY

(8) *Insert Legal Entity and State or Country (e.g., a corporation or citizen of Japan)* — (8) a Norwegian company of NORWAY

(hereinafter designated as the Assignee) the entire right, title and interest for the United States, its territories, dependencies and possessions, in the invention known as

(9) *Insert Identification of Invention, such as Title, Case Number or Foreign Application Number* — (9) Methods for patterning polymer films, and use of the methods

.....

for which the undersigned has (have) executed an application for patent in the United States of America

(10) *Insert Date of signing of Application, or filing date and Serial No., if known* — (10) Said application having been ~~executed~~/filed on Jan. 9, 2001 (and assigned Serial No. 09/720,259)

1) The undersigned agree(s) to execute all papers necessary in connection with this application and any continuing or divisional applications thereof and also to execute separate assignments in connection with such applications as the Assignee may deem necessary or expedient.

2) The undersigned agree(s) to execute all papers necessary in connection with any interference which may be declared concerning this application or any continuing or divisional applications thereof and to cooperate with the Assignee in every way possible in obtaining evidence and going forward with such interference.

3) The undersigned agree(s) to execute all papers and documents and perform any act which may be necessary in connection with claims or provisions of the International Union for Protection of Industrial Property or similar agreements.

4) The undersigned agree(s) to perform all affirmative acts which may be necessary to obtain a grant of a valid United States patent to the Assignee.

5) The undersigned hereby authorize(s) and request(s) the Commissioner of Patents and Trademarks to issue any and all Letters Patents of the United States resulting from this application or any continuing or divisional applications thereof to the said Assignee, as Assignee of the entire interest, and hereby covenants that he has (they have) full right to convey the entire interest herein assigned, and that he has (they have) not executed, and will not execute any agreement in conflict herewith.

6) Assignor hereby further assigns to Assignee all claims and causes of action for infringement of the patent rights assigned herein, including the right to sue for, and collect damages for, any and all acts of past and future infringement.

7) The undersigned hereby grant(s) the law firm of **Jacobson, Price, Holman & Stern, PLLC**, 400 Seventh Street, N.W., Washington, D.C. 20004, the power to insert on this assignment any further identification which may be necessary or desirable in order to comply with the rules of the United States Patent and Trademark Office for recordation of this document.

In witness whereof, executed by the undersigned on the date(s) opposite the undersigned name(s).

Date 2000 12 23	Name of Inventor	Olle Inganäs (typed name)	Olle Inganäs (signature)	(SEAL)
Date 2000 DEC 23	Name of Inventor	Tobias Nyberg (typed name)	Tobias Nyberg (signature)	(SEAL)
Date 2001-01-16	Name of Inventor	Tomas Granlund (typed name)	Tomas Granlund (signature)	(SEAL)
Date _____	Name of Inventor	_____ (typed name)	_____ (signature)	(SEAL)
Date _____	Name of Inventor	_____ (typed name)	_____ (signature)	(SEAL)

This assignment should preferably be signed before a United States Consul if signed abroad, or a Notary Public if domestically signed. If not, then the execution by the inventor(s) should be witnessed by at least two witnesses who sign here:

☐ Additional inventor's names and signatures on a separate sheet.

Witness _____

Witness _____

LAW OFFICES OF

JACOBSON, PRICE, HOLMAN & STERN

PROFESSIONAL LIMITED LIABILITY COMPANY

THE JENIFER BUILDING

400 SEVENTH STREET, N.W.

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